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Observations on the Rare Earths:
The Purification of Erbium, with special Reference to the Separation from Yttrium;
The Atomic Weight of Erbium.

OBSERVATIONS ON THE RARE EARTHS: THE PURIFICATION OF ERBIUM, WITH SPECIAL REFERENCE TO THE SEPARATION FROM YTTRIUM; THE ATOMIC WEIGHT OF ERBIUM

BY

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A. B. Hope College, 1913
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I. HISTORICAL.- The history of the elements of the yttrium group of rare earths dates back to the discovery of an oxide called yttria, which was found by Gadolin[1] in the mineral now known as gadolinite, in the year 1794. It was not until 1843 that yttria was found to be a mixture. In that year Mosander[2] came to the conclusion that yttria was composed of at least three oxides. He named yttria, erbia, and terbia as the components of the original oxide. His erbia, however, probably contained the terbia of today, since he says that the oxide is yellow on ignition in air but white on ignition in hydrogen, and that the salts are colorless. His terbia gave rose-colored salts.

Berlin[3], in 1860, obtained only two oxides from old yttria, colorless yttria and a rose-colored oxide which he called erbia. He could not find the yellow erbia of Mosander. Four years later Popp[4] claimed that yttria was not a mixture, but that the erbia of Berlin was a mixture of cerite oxides. Bahr and Bunsen[5] however, in 1866 confirmed the results of Berlin, recognizing yttrium salts as colorless and erbium salts as rose-colored and giving an absorption spectrum different from that of didymium.

Shortly afterward Delafontaine[6] asserted that crude yttria might be separated into the three oxides of Mosander. On the

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[1] Sv. Vet. Akad. Handl., p.137 (1794); Crell's Ann., I, 313 (1796)

[2] J. pr. Chem., 30, 288 (1843)

[3] Förhandl. Scand. Naturf. 8 Möde, Kjobenhavn, 448 (1860)

[4] Ann. Chemie, 131, 179 (1864)

[5] Ann. Chemie, 137, 1 (1866)

[6] Ann. Chemie, 134, 99 (1865); 135, 188 (1865)

other hand Cleve and Höglund[1], using the method of the partial decomposition of the nitrates by heat, as originated by Berlin[2] and as modified by Bahr and Bunsen[3], could find only erbia and yttria. Marignac[4] was later able to find terbia in the fractions of the nitrate fusion, and Delafontaine[5] prepared it from the less soluble fractions of a sodium double sulphate separation of yttria, by fractionating with oxalic acid and later with formic acid.

Delafontaine[6] also found a yellow earth in the soluble fractions of the sodium double sulphate separation. This had a various career until the absorption band by which Delafontaine recognized it was found to belong to the element now known as holmium. In 1879 Humpidge and Burney[7] published some work which was prefaced with a review of the earlier work on erbium. Only yttrium, terbium, and erbium were known at this time, the ytterbium announced by Marignac[8] not having been confirmed.

Marignac's ytterbia had been obtained by the nitrate fusion method and in 1880 Nilson[9], using the same method, confirmed the existence of this oxide. Later Nilson[10] isolated scandia from his ytterbium material. Cleve[11] studied some of Nilson's erbium

[1] Bull. Soc. Chim. Paris, 18, 193 (1872)
[2] Loc. cit.
[3] Loc. cit.
[4] Ann. Chim. Phys.,(5) 14, 247 (1878)
[5] Ibid.,(5) 14, 238 (1878)
[6] Loc. cit.
[7] J. Chem. Soc. 35, 111 (1879)
[8] Compt. rend., 87, 578 (1878). Chem. News, 38, 213 (1878)
[9] Ber., 12, 550 (1879); 13, 1430 (1880)
[10] Ibid., 12, 554 (1879); 13, 1439 (1880)
[11] Compt. rend., 89, 478 (1879); Chem. News, 40, 125(1879)

from which ytterbium and scandium had been removed, and after long fractionation obtained material whose solution was tinged orange and also some fractions which were tinged violet. He concluded that this indicated the presence of two new elements, the first of which he named holmium and the other thulium. Soret[1] had also detected the presence of these elements. Since this time the old erbia of Berlin, which had proven to be the mother substance of four new elements, has been no further resolved. The two elements which yet remained to be discovered to complete the yttrium group as it is accepted today, were dysprosium and lutecium. The former of these was found by Lecoq de Boisbaudran[2] in holmium material and the latter was separated by Urbain[3] from ytterbium.

Krüsz[4], fractionating erbium material by means of aniline, could not obtain fractions of constant atomic weight, and the difference in intensity of certain lines in the absorption spectra of their solutions led Krüsz and Nilson[5] to believe that erbium, and holmium, thulium, and dysprosium as well, were still complex. Hofmann and Burger[6], however, further studied the material used by Krüsz and obtained no results which put the individuality of erbium into question. They also presented arguments refuting the conclusions drawn by Krüsz and Nilson from variations in the absorption spectra. Lately Eder[7] has concluded

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1. Ibid., 89, 1062 (1879); Ibid., 40, 147 (1879)
2. Ibid., 102, 1003 (1886); Ibid., 53, 265 (1886)
3. Ibid., 145, 759 (1907)
4. Z. anorg. Chem., 3, 353 (1893)
5. Ber., 20, 2134 (1887)
6. Ber., 41, 308 (1908)
7. Sitzb. Akad. Wiss. Vienna, IIa 124; C.A. 10, 2663 (1916)

from arc spectrum studies that erbium is complex and that its resolution may be expected with further investigation. Willand and James[1] confirm the opinion of Hofmann and Burger as to the individuality of erbium as the result of a long-continued fractional crystallization of the bromates, in which there was no change in the absorption spectrum. It may be added that the work done in this laboratory on the yttrium group earths has never furnished any indication that erbium is other than an individual.

Determinations of the atomic weight of erbium are numerous but these made by the earlier workers are of little value. This is due to the fact that the erbium material contained other elements not yet discovered at the time the determinations were made. In 1908 Hofmann and Burger[2] found the value 167.40 as the mean of four determinations of the ratio Er_2O_3: $Er_2(SO_4)_3$.

In 1910 Hofmann [3] further purified the material used by Hofmann and Burger and obtained as a mean of three determinations of the oxide sulphate ratio the value 167.68, which is the basis for the value given in the international table, 167.7.

II. GENERAL DISCUSSION OF METHODS FOR THE PURIFICATION OF ERBIUM.-- Earlier workers have usually attempted to separate erbium from the other members of the yttrium group by methods depending upon the difference in basicity of the elements or

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1. J. Am. Chem. Soc., 38, 1198 (1916)
2. Loc. cit.
3. Ber., 43, 2631 (1910)

methods depending upon comparatively slight differences in solubility of various salts. The considerable difference in basicity between erbium and yttrium made it possible to effect a fairly rapid separation of these elements but the slight difference in basicity between erbium and terbium, dysprosium, and holmium on the one hand; and thulium, ytterbium, and lutecium on the other, made the separation from these elements a tedious process.

In this laboratory it has been found an excellent plan to subject the elements of the yttrium group to fractional crystallization as bromates, as proposed by James[1], until fractions are obtained which contain no more than two or three of the members of the group.[2] This is particularly successful in the case of erbium. Owing to the preponderance of yttrium and erbium in most crude yttrium group material, and the fact that they are adjacent in the order of solubility of the bromates, it is possible to obtain, after a relatively short series of crystallizations, material containing yttrium and erbium with no detectable quantities of any of the other rare earths.

The work described in the following paragraphs forms part of a study undertaken in this laboratory to determine the relative efficiencies of a number of methods that have been proposed for the separation of erbium from yttrium, using material obtained by the bromate fractionation as described in the preceeding paragraph. The erbium-yttrium mixture was obtained by

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[1] J. Am. Chem. Soc., 30, 182 (1908)

[2] Engle and Balke, Ibid, 39, 53 (1917)

combining several fractions from a bromate series run by Dr. E.W. Engle. The original source of the material and the method of separation from the other elements of both the cerium and yttrium groups are described in a publication on a research carried out by Engle and Balke[1]. The greater part of the material gave a value of 108.5 as the mean atomic weight by the permanganate titration method of Gibbs[2]. This is approximately equivalent to 25% erbium. A small part of the material gave a mean atomic weight of 104, which is approximately equivalent to 19% erbium. Neither the original material nor any part of it obtained by the methods employed as later described , showed the presence of any elements of the rare earth group except yttrium and erbium.

The progress of separation was studied by the color of the oxides, by the absorption spectra of the solutions, and by the atomic weights. The method used for obtaining the atomic weight for control purposes was that of Gibbs. In the yttrium rich fractions of the various series it was quite feasible to judge fairly small differences in erbium content by the color of the oxide and the depth of the absorption bands of standard solutions. Wherever erbium was present in amounts greater than perhaps 5% it was found difficult to judge closely the difference in composition of various fractions by this method. Since the atomic weights of the two elements are so widely separated, the mean atomic weight of a fraction gave a good measure of the composition except when only a very small quantity of one

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1. Loc.cit.
2. Am. Chem. J., 15.546 (1893)

element was present.

III. THE METHOD OF WIRTH.-- Some work done by Wirth[1] on the solubility of the rare earth oxalates in sulphuric acid suggested a possible means of separation. Wirth says that yttrium oxalate is converted to the sulphate by sulphuric acid of specific gravity 1.186, while erbium oxalate is soluble without decomposition in acid of the same concentration. Accordingly, 20 grams of the oxalate of material containing 25% erbium was shaken with 500 c.c. of sulphuric acid, whose specific gravity was roughly determined to be 1.21, at room temperature until nearly all the oxalate dissolved. The clear solution was poured off after the sulphates had just commenced to precipitate and was allowed to stand for several days. The crystals which were obtained were pink, thus evidently not free from erbium, and the mother liquor contained only traces of rare earth. It seemed that no separation could be effected in this way.

IV. THE BASIC CHLORIDE METHOD OF DROSSBACH.-- Drossbach[2] treated the neutral chloride solution of a mixture containing principally erbium and yttrium with oxide of the same composition and effected in this way a strikingly rapid separation. Thirty grams of oxide of a mean atomic weight of 104, which is equivalent to 19% erbium, was dissolved in hydrochloric acid. To the nearly neutral solution 24 grams of oxide was added

1. Z. anorg. Chem., 76, 174 (1912)
2. Ber., 35, 2826 (1902)

and the mixture evaporated to a syrup and allowed to remain on the steam bath for forty-eight hours. At the end of this time the liquid was diluted, the solution filtered off, and the residue dissolved in hydrochloric acid. The atomic weight of the portion in solution was 95.9 and that of the residue was 110.6. These results, while showing a good separation, are not nearly as good as are claimed for the method by Drossbach.

V. FRACTIONAL PRECIPITATION WITH POTASSIUM COBALTICYANIDE.-- James and Willand[1] have studied a number of methods for the separation of erbium and yttrium. Fractional precipitation of the cobalticyanide was found by them to give very satisfactory results. Fifty-eight grams of erbium-yttrium oxide with an atomic weight of 108.5 was used in this experiment. The cobalticyanide used in this series was prepared by treating a solution of cobalt nitrate with a solution of potassium cyanide until the precipitate redissolved. Air was then passed through the solution for about an hour, after which bromine was added to precipitate the nickel which was present. The solution was filtered off, acidified with acetic acid, and evaporated to crystallization. The material so obtained was once recrystallized from water. The solution of the nitrate with a slight excess of nitric acid was diluted to about 1500 c.c. and boiled, while 220 c.c. of a 10% solution of potassium cobalticyanide were added drop by drop. A very slight precipitate formed, which was probably due to the presence of copper in the solution. This was filtered off, and the solution boiled while a

[1] J. Am. Chem.Soc., 38,1198 (1916); 38, 1497 (1916)

second 220 c.c. portion of the reagent was added drop by drop. Boiling was continued after the addition of all the reagent. After some time a slight precipitate appeared which rapidly increased in volume. This would indicate supersaturation but the same diddiculty in getting precipitation to start was experienced with every fraction, notwithstanding the fact that in the later fractions a small amount of the precipitate from the preceeding fractionwas usually introduced after about half of the reagent had been added. It is possible that a difference in crystallographic form exists between the precipitates at various stages of the precipitation. This might be due to a variation in the amount of water of hydration or some other difference in the composition of the precipitate. But the difficulty in securing a uniform rate of precipitation appears to offer serious objections to the method. A close approach to equilibrium between the solution and the precipitate cannot be hoped for under these conditions.

Fractions 3,4, and 5 were run in the same manner as 1 and 2, except that a precipitate was secured in each case. Fractions 6 and 7 were run at a volume of one liter. In 8,9, and 10, twice the amount of reagent was used and the volume was 700 to 800 c.c. Fraction 11 was precipitated from a volume of 250 c.c. with a double portion of reagent. Fraction 12 was precipitated with ammonium hydroxide. In some of the later fractions alcohol was added to the boiling solution to hasten the beginning of precipitation. In no case, however, was a uniform rate of precipitation secured.

The precipitates were crystalline, and filtered and washed well. They were decomposed by boiling with 15 to 20% sodium hydroxide solution, the hydroxides being washed on the filter and subsequently dissolved in nitric acid, from which solution the oxalates were precipitated by means of oxalic acid. Samples for analysis were purified by a second precipitation with oxalic acid. The atomic weights were determined by the permanganate method. The data for the series follows.

Fraction No.	Wgt. gms.	Per cent of total	Atomic wgt.
1 and 2	11.2	19.3	123.0
3	6.7	11.6	119.5
4	6.2	10.7	---
5	6.8	11.7	113.0
6	6.7	11.6	---
7	5.4	9.3	100.3
8	8.8	15.0	---
9	2.7	4.7	91.0
10	1.1	2.0	---
11	0.4	0.7	---
12	2.0	3.4	89.2

It will be noticed that the fall in atomic weight in the earlier fractions is slower than in the later. This is probably due in part at least, to the greater difficulty experienced with the rate of precipitation in these fractions. The oxide of fraction 10 has a very faint pink color and shows only a faint absorption. No pink color could be detected in the oxide

of fraction 12. It is to be noted that while the rise in the amount of erbium in the earlier fractions is not all that might be hoped for the latter part of the series shows a very good separation. The last fractions, though it is true they represent only a small portion of the original material, yielded very nearly pure yttrium.

VI. FRACTIONAL PRECIPITATION WITH SODIUM NITRITE.-- Sodium nitrite has been used by several workers in the rare earths but the method employed has varied somewhat. Hofmann and Burger[1] treated their material with an excess of sodium nitrite and evaporated to dryness. James[2] and his co-workers add the sodium nitrite solution gradually to the boiling solution of the rare earth salts. As was pointed out by Hopkins and Balke[3] it has been found a better plan to add the whole of the sodium nitrite solution which is to be used for one fraction to the dilute solution of the earth salt in the cold and subsequently boil the solution to cause precipitation. It is evident that this insures a better opportunity for equilibrium to be established.

The material used in the first series was nitrate, equivalent to 75 grams of oxide, with an atomic weight of 108.5. This was dissolved in water and the solution diluted, in a ten litre flask, to six or seven litres after neutralizing as nearly as possible with ammonium hydroxide. A solution of 15 grams of

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1.Ber., 41, 308 (1908)
2. J. Am. Chem. Soc. 36, 1419 (1914)
3. Ibid, 38, 2332 (1916)

sodium nitrite was added and the solution boiled for one hour by passing in live steam. Only a very slight precipitate was obtained. This is the usual experience in this method. Apparently a quantity of sodium nitrite is used up in establishing the proper condition of acidity in the solution. The solution was allowed to cool, a second portion of sodium nitrite was added and the solution boiled for another hour. The precipitate which formed was filtered off, washed somewhat with hot water, and dissolved in dilute nitric acid, from which solution the earth was precipitated with oxalic acid. This procedure was repeated until fourteen fractions were obtained. The amount of sodium nitrite used to precipitate a fraction was gradually increased up to 50 grams. The time of boiling was one hour and the volume of the solution varied from six to eight litres. All of the earth in the solution was removed by sodium nitrite. The precipitates settled well and could be washed on the filter without difficulty.

Samples of the fractions were purified by a second precipitation with oxalic acid and the atomic weights were determined by the permanganate titration method. In order to determine whether this method of preparing the samples gave material of sufficient purity, samples from fractions 2 and 12 were further purified by two precipitations with ammonium hydroxide and oxalic acid, the two reagents being used alternately. The sample from fraction 2 gave a value 0.4 higher, while that from 12 gave a value 0.8 lower, than the less carefully purified oxalate. It seemed thus that if some care were exer-

cised in washing the nitrite precipitate free from the solution, which toward the end of the series contained considerable quantities of sodium salts, the oxalate precipitate could be sufficiently purified for control atomic weight determinations by one further precipitation with oxalic acid. The tabulated data for the first series follows:

Fraction No.	Wgt. gms.	Per cent of total	Atomic weight
1	2.1	3.0	129.4
2	5.0	6.7	126.7
3	4.4	6.0	126.1
4	3.2	4.0	126.0
5	5.6	7.5	120.5
6	6.7	9.0	119.5
7	9.3	12.4	115.3
8	6.4	8.5	110.1
9	10.4	14.0	104.8
10	8.8	11.7	97.8
11	8.2	11.0	93.0
12	3.5	5.0	90.6
13	1.1	1.5	89.6
14	0.9	1.2	90.4

The results of this series made it seem worth while to apply the method to a mixture richer in erbium. For the second series the material from fractions 1 to 6 of the first series was used.

This comprised 25 grams of material of which the mean atomic weight, by calculation, was 123.7. The oxide was dissolved in nitric acid, and the excess acid nearly neutralized with ammonium hydroxide. The series was run like the first one except that the volume was from two to three litres. For the first fraction the solution was boiled over a burner but even with these small volumes it was found more desirable to boil the solution with a current of steam. With the volume of solution used a slight precipitation usually occurred soon after the addition of the reagent, before the solution was heated. The boiling was continued for one hour in all cases except with the last fraction when the solution was boiled for an hour and a half to insure complete precipitation of all the earth remaining in the solution. The tabulated data for the series follows:

Fraction No.	Wgt. gms.	Per cent of total	Atomic weight
1	4.8	19.0	142.9
2	6.3	24.9	140.2
3	5.6	22.1	128.8
4	3.8	15.0	---
5	3.9	15.4	---
6	0.9	3.6	91.3

Some conclusions may be drawn from the data for the two series as to the efficiency of this method of separation and the number of fractions into which a series should be divided. In the first series the first seven fractions comprise 44% of the

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

total material and would if combined have a mean atomic weight of 122.1, which is a rise of 13.6 over the original. In the second series the first two fractions comprise 44% of the total material and these combined would have a mean atomic weight of 141.4, which is a rise of 17.7 over the original. Up to this point, then, the method is increasing in efficiency with the rise in the proportion of erbium in the mixture. A comparison of the two series would also seem to indicate that nothing is to be gained by dividing the series into a large number of fractions. In the second series the first fraction includes 19% of the total and shows a rise of 19 in atomic weight, while the first fraction of the first series represents only 3% of the total and shows a rise of 21. The last fraction of the second series, representing a greater percentage of the total material in the series than the last two fractions of the first run has an atomic weight but one unit higher than these. The slight difference in value between the first two fractions, in the second series, and the sharp break after the second fraction, are also worthy of note.

n general the results of these two series indicate that the method of precipitation with sodium nitrite affords at least as rapid a separation of erbium and yttrium as does precipitation with potassium cobalticyanide and has the further advantage of greater ease of manipulation, both in the fractionation itself, and in the recovery of the fractions. Sodium nitrite is furthermore a more readily available reagent than potassium cobalticyanide.

VII. FRACTIONAL DECOMPOSITION OF THE NITRATES.-- The methods above described together with the ferricyanide precipitation recommended by Grant and James[1], are probably the best of those more recently proposed for the separation of erbium and yttrium. The method most used for this purpose by the earlier workers, however, was the nitrate fusion, which was originated by Berlin[2]. In order to make an actual comparison of these newer methods with the classic separation, it was decided to carry out the nitrate fusion for a few operations on material of the same composition as that used in the study of the other methods.

The method is carried out as follows. The solution of the nitrate is evaporated in a porcelain casserole until brown fumes begin to appear. It is desired to carry the decomposition to a point where all the fused material will dissolve in a small quantity of hot water, the basic nitrate crystallizing from the solution on cooling. If carried too far, the decomposition yields a more highly basic salt, which is insoluble in water. According to Bahr and Bunsen[3] yttrium is most rapidly eliminated if the less basic salt is obtained. Unless there is only a small quantity of material it is best to pour the melt upon the polished surface of a marble slab. After cooling, the glass is returned to the casserole and dissolved in hot water. The cooled solution is then removed from the crystals of basic nitrate, by suction on a filter if necessary, and the fusion repeated on the two fractions. The solution from the less basic fraction is combined with the crystals from the more basic fraction

[1] J. Am. Chem. Soc., 39, 933 (1917)

[2] Loc. cit.

[3] Loc. cit.

and the separation is then run as a series.

In order to have about equal amounts of material in all the fractions of the series, the original 300 grams of oxide dissolved in nitric acid was fused three times, each time removing the basic salt that separated and setting it aside. The four portions were then run as a series and carried through two operations. It is evident then that at the end of this time the fraction toward the erbium end had been carried through only three fusions, the second one through four, and the other four fractions through five fusions. All the fractions but the first were about equal in bulk, the first being rather smaller than the others. The atomic weight of the original material was 108.5 and the six fractions were found to have atomic weights as follows:

4 A.	4 B.	4 C.	4 D.	4 E.	4 F.
159.3	141.4	119.7	118.1	102.6	91.9

These results indicate that the nitrate fusion furnishes a method of separating erbium and yttrium that is much simpler to operate and that is much more efficient than the best of the other methods proposed for the purpose. Whether it would completely free either of the elements from the other is not shown by this data. The fact that it has been used in nearly every atomic weight study of erbium recommends it for the purification of this element at least.

VIII. PREPARATION OF MATERIAL FOR THE ATOMIC WEIGHT STUDY.-- The present accepted value for the atomic weight of erbium was determined by Hofmann[1] by the synthesis of the sulphate from the oxide. His material was probably the purest obtained up to that time. Work done in this laboratory has raised serious objection to the oxide-sulphate ratio, however, and it was deemed advisable to study the applicability of the oxide-chloride ratio heretofore used by Egan and Balke[2] and Hopkins and Balke[3] for yttrium, and by Engle and Balke[4] for dysprosium. It was thought possible that in the course of the investigation light might be thrown upon the value of the ratio and the general tendency it exhibits to give higher results than are obtained by other ratios.

There was at hand a small series of erbium-yttrium material taken from certain fractions of a bromate series which were very rich in erbium and far removed from fractions showing holmium, on the one hand, and thulium, on the other. This material had been further purified by running it for some time as a nitrate fusion series, according to the method described earlier in this paper[5]. By running this series somewhat longer it seemed that erbium material of a very high degree of purity might be obtained. The series was run in from six to eight fractions. After thirty-two operations the atomic weights of all the fractions except the second and third were determined by the permanganate method. The results were as follows:

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1. Ber., 43, 2361 (1910)
2. J. Am. Chem. Soc., 35, 365 (1913)
3. Ibid., 38, 2332 (1916)
4. Ibid., 39, 53 (1917)
5. This work was carried out by Dr. E.W. Engle.

32 H	32 I	32 K	32 L	32 M	32 N	32 O	32 P
166.31	---	---	166.17	164.68	163.75	154.63	119.90

The first and fourth fractions have practically the same atomic weight and it may be concluded that fractions 1 to 4 have the same composition within the limits of accuracy of the control analysis. It may be stated that the relative values could be obtained with good accuracy by this method. Duplicate analyses of the same fraction rarely differed by more than 0.1 in the atomic weight. The fact that the atomic weight is more than a unit less than the accepted atomic weight of erbium cannot be taken as indicating the presence of considerable yttrium since this method does not ordinarily give absolute values. This is born out by the fact that the values later obtained by the oxide-chloride ratio were much higher. This close agreement of the atomic weights of the first and fourth fractions indicated that a very high degree of purity had been attained. It is not to be considered certain, however, that this material is absolutely free from yttrium. An attempt was made to detect the presence of yttrium by a study of the arc spectrum. This could not be accomplished with the apparatus at hand. The fractionation was carried through two more operations and the fractions 34 K, 34 L, and 34 M used in the study of the oxide-chloride ratio.

IX. PREPARATION OF REAGENTS USED IN THE DETERMINATION OF THE RATIO Er_2O_3:2 $ErCl_3$.---

Water.-- Ordinary distilled water was redistilled from

alkaline permanganate in the still used for preparing conductivity water.

Oxalic acid.-- The best obtainable oxalic acid was dissolved in water and the solution filtered. After the addition of a small amount of nitric acid the solution was evaporated in a porcelain dish till crystals commenced to form on the surface. The solution was then poured into a Jena flask and cooled rapidly with constant agitation. A mass of very fine crystals was obtained which was drained in a porcelain centrifuge. This material was recrystallized from conductivity water and redistilled nitric acid with rapid cooling and centrifugal drainage as before. The third recrystallization was from conductivity water. These crystals were centrifugally drained and air dried, being covered with filter paper to prevent the access of dust. Twenty grams of the oxalic acid left only a slight visible trace of residue when ignited in a porcelain dish.

Nitric acid.-- "Chemically pure" nitric acid was distilled from a quartz bulb into a quartz receiver. The middle one-third was used.

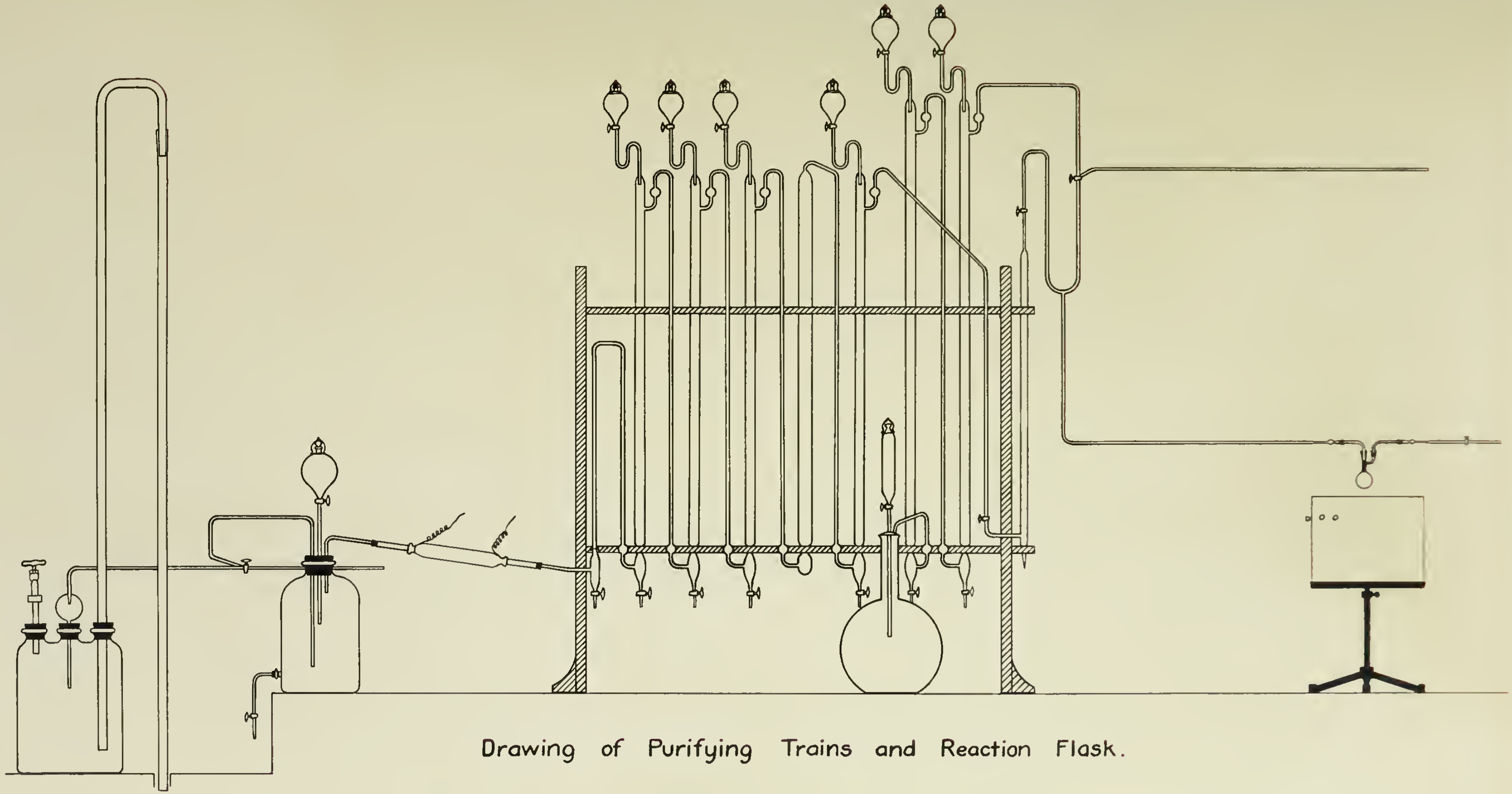
Hydrochloric acid.-- "Chemically pure" hydrochloric acid was heated in a quartz bulb and the vapors absorbed in conductivity water in a quartz receiver.

Hydrochloric acid gas.-- The gas was generated by dropping "chemically pure" sulphuric acid into "chemically pure" hydrochloric acid. The gas was purified by passing through two vertical towers, each one metre high and 2.5 cm. in diameter and filled with glass beads wet with sulphuric acid which had prev-

iously been heated at the boiling point for some time to remove any volatile matter which might be present. Solid glass connections or dry ground joints were used in this purifying train.

Ammonia.-- Ammonia was prepared as used by warming the concentrated solution of "chemically pure" ammonia and passing the vapors over the solution with which the ammonia was to react.

Air and atmospheric nitrogen.-- A current of atmospheric nitrogen free from moisture, carbon dioxide, and the impurities of the laboratory atmosphere was provided by part of the apparatus shown in the drawing. The discharge pipe of a filter pump was passed through a rubber stopper into a large Wolff bottle. Through another neck of the bottle passed a glass tube of large bore and 130 cm. in height, with the top bent in the form of a "U" and fitted into a larger glass tube leading to the sink. The water and excess air drawn into the bottle by the filter pump was thus forced out through the vertical tube and a constant pressure of air equal to the weight of the column of water in the tube provided. The passage of the air through the filter pump gave it a preliminary scrubbing. The air was drawn off through the third neck of the Wolff bottle, which was fitted with a Hopkins distilling head connected through a rubber connection to a two-way stopcock. One lead from the stopcock ran into the second bottle shown in the drawing. This bottle contained ammonia solution through which the air bubbled, taking up enough ammonia vapors to remove the oxygen as the mixed gases passed over hot copper gauze. The gauze was heated in a



Drawing of Purifying Trains and Reaction Flask.

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quartz tube which was placed within a silica tube wound with "nichrome" wire and covered with several thicknesses of asbestos paper cemented with "water glass". After passing through the quartz tube the oxygen free air and ammonia were led through a trap provided to catch moisture, into the first tower of the purifying train. This tower was 2.5 cms. in diameter and 60 cms. high and contained glass beads wet with 45 to 50 percent sulphuric acid. Leaving this tower the gas passed through a similar one containing a nearly saturated solution of silver sulphate acidified with sulphuric acid and one containing sulphuric acid. Next was a tower 4.5 by 60 cms., containing solid potassium hydroxide in sticks, succeeded by a tower for concentrated sulphuric acid similar to the first one and a tube, 2 by 60 cms., filled with glass wool into which phosphorus pentoxide had been sublimed. Leaving this tube the gas passed into the reaction flask, as shown in the diagram. This purifying train gave atmospheric nitrogen free from impurities except a slight amount of hydrogen and some carbon dioxide. The proceedure of converting the oxide to the anhydrous chloride as practiced by Hopkins and Balke, and Engle and Balke, was subsequently modified, however, so that oxygen free air was not used.

Air was purified in the same way except that the lead from the two-way stopcock was connected directly to the first tower. The train was similar to the one shown in the drawing and mounted on the front of the same wooden frame.

The two taller towers shown in the drawing constituted the drying train for hydrogen chloride gas. The generator is shown

connected to the first of these two towers. The whole apparatus was so arranged that any of the reagents, except the potassium hydroxide and the phosphorus pentoxide. might be renewed without the admission of the laboratory air. Rubber stoppers were used in the Wolff bottle, in the bottle containing ammonia solution, and in the connections with the quartz tube containing the copper gauze. All connections in the trains were of solid glass. The tubes coming from the ends of the air and nitrogen trains were connected through a "Y" tube not shown in the drawing, to the tube leading to the reaction flask. The lead from the hydrogen chloride generator was provided with a two-way stopcock, so that the gas might be conducted through a "Y" tube into the main lead to the furnace or into a waste line leading to the hood.

The whole apparatus was similar in principle and in most details of construction to that used in previous atomic weight researches carried on in this laboratory.

X. PREPARATION OF THE ERBIUM OXIDE USED IN THE DETERMINATIONS.

The material used was taken from the nitrate fusion series previously described. The solution of the nitrate was filtered, acidified with nitric acid, and the earth precipitated with ammonium hydroxide by distilling ammonia vapors into the flask containing the solution. Sufficient nitric acid was added to insure the presence of a considerable amount of ammonium nitrate. This helped to give a precipitate which would settle and allow of washing by decantation without becoming colloidal, as is the

case when insufficient electrolyte is present. The precipitation was made in a three litre Jena flask at a volume of about 1500 c.c. Even in the presence of considerable ammonium nitrate some very fine particles always remained in suspension unless a much longer time was given for settling than was deemed advisable on account of the solvent action of the more or less alkaline liquid upon the glass. This occasioned quite a little loss in the washing process. For this reason the number of washings was usually limited to four, a sufficient portion of the supernatant liquid being removed each time so that less than 1% of the total amount of dissolved material present in the mother liquor would be left at the end of the washing.

The precipitate was next dissolved in nitric acid and the solution diluted to about 1500 c.c., well acidified with nitric acid, and heated to boiling. A solution of oxalic acid heated to the boiling point, was added until precipitation of the oxalate just commenced. Some excess was added but care was taken to avoid causing rapid precipitation. The solution was then allowed to cool, whereupon the oxalate separated from the cooling solution in a flaky crystalline form. In some cases the cooling was hastened by shaking the flask in a stream of water from the tap. The oxalate precipitate was transferred to a quantitative filter and thoroughly washed. Since the samples were small it was thought possible to obtain as thorough washing on the filter as by decantation. After drying at 110°-120° the oxalates were ignited in a platinum crucible over a Bunsen burner. The oxide was dissolved in nitric acid and the earth

material subjected to a second precipitation with ammonia and with oxalic acid from ordinary distilled water. The double precipitation was carried out a third time, using conductivity water and redistilled nitric acid. Before the final precipitation with oxalic acid the solution was in most cases filtered to insure the removal of any solid particles that might be present.

The finally purified oxalate was ignited in a platinum crucible supported on a "nichrome" triangle in an electrically heated furnace made by winding an alundrum core with coiled "nichrome" wire. The winding was plastered over with alundum cement and the core packed with kiesel-guhr in a light sheet-metal cylinder. The surface of the packing was covered with alundum cement with a water-glass binder and the core was provided with a set of porcelain rings so that the furnace might be entirely closed. The winding was in two equal parts and so arranged that a current could be passed through the entire winding, through either half, or through both halves in parallel. By the use of outside resistance the temperature could be regulated between room temperature and as high a point as can be reached with "nichrome" wire. Temperatures up to 350° were read directly on a thermometer the bulb of which was lowered into the furnace. For the higher temperatures an ammeter was placed in the circuit and the furnace temperature calibrated at a number of different readings of the instrument. A given temperature could then at any time be duplicated within a few degrees, by adjusting the reading of the ammeter by means of

the outside resistance. The temperature at which the oxide was heated and the duration of the ignition are shown in the table of data. The oxide invariably showed a buff color at the contact surface with the platinum and the air. Underneath the surface the color was a pure pink.

XI. THE REACTION.-- The method of converting the oxide to the chloride was quite similar to that described for yttrium by Egan and Balke. The quartz reaction flask was somewhat smaller, being of 25 c.c. capacity. The oxide was transferred to the weighed flask while hot, after which the inlet and outlet tubes were immediately inserted and their caps adjusted. The flask was hung in the balance case till equilibrium of conditions was established. In most cases weighing could be commenced an hour and a half or two hours after the flask was placed in the case, particularly if care was taken to avoid electrifying the flask. A half hour before weighing was begun one of the caps was loosened for an instant to equalize the pressure in the flask with that of the atmosphere. In no case did the oxide show any tendency to absorb moisture or carbon dioxide from the air.

The balance used is one made by Ruprecht and is used exclusively for atomic weight work. Weighings were made throughout by substitution, a flask of nearly the same shape,size, and weight being used as a tare. The weights used were carefully calibrated to .01 mg.The weights of the oxide and chloride were reduced to vacuum standard, the specific gravity of the

brass weights being taken as 8.4, of the platinum weights as 21.5, of the oxide as 8.64, and of the chloride as 4.1. The value for the oxide is taken from Nilson and Pettersson[1]. These authors do not state how their oxide was prepared but while there is probably some difference in the specific gravity of oxide prepared by the ignition of different salts, it is not probable that this difference would prove sufficient to materially effect the vacuum correction. The specific gravity of the chloride could not be found in the literature. It was roughly determined by transferring the globule of fused chloride, at the end of two runs, from the reaction flask to a pycnometer in which its specific gravity was determined against benzene, the latter being referred to water. The two determinations gave a value of 4.1 0.2. This was considered sufficiently accurate for the purpose in view.

After weighing the flask with the oxide , the oxide was dissolved in hydrochloric acid. In most cases pure hydrochloric acid was added directly to the oxide in the flask but in one case pure water was added and hydrogen chloride was passed in from the purifying train. Solution took place slowly on warming the flask. No effervescence or spattering was noticed in any case. There always remained in the chloride solution a very small quantity of light colored solid residue, partly in suspension and partly on the bottom of the flask. There was some question as to the nature of this but the quantity was never

[1] Ber. 13, 1459 (1880)

sufficient to make an analysis possible. Every precaution was taken to keep the sample free from foreign matter and no residue was noticed whenever the oxide was dissolved in the platinum crucible in the process of purification. It was also noticed that during the subsequent fusion of the chloride a slight scum always formed on the surface of the molten salt. After the chloride had cooled this scum was greyish in color. It did not appear to dissolve when water was added to the chloride. This residue may have been platinum which had distilled into the oxide during the prolonged ignition, for in the case of the eighth determination, in which the ignition had been the longest, small black particles were found to have collected in the solution of the fused chloride after standing for several days. The solution was filtered through a quantitative paper and the filter ignited. The ash was dissolved in aqua regia. After evaporating to dryness the residue gave a very distinct, though not a heavy, test for platinum with potassium iodide solution. The solution of the fused chloride from the seventh determination was kept saturated with hydrogen sulphide for two days. After allowing the solution to stand several more days it was filtered, and the filter ash tested for platinum. The reaction was positive but the amount of platinum present was much less than in the previous case. The oxides for these two determinations had been ignited much longer than most of the others so that it is hardly probable that the residue after the solution of the oxide in hydrochloric acid may be accounted for as platinum alone. As was pointed out, the residue was of

a light color. Finely divided platinum should be black. It is also possible that the hot oxide reacted with the quartz of the flask, the inside surface of which was etched by reaction with basic chloride in another series of determinations. Any silicate which was formed would be decomposed by hydrochloric acid[1] so that if the residue had this origin it would not affect the value of the ratio, being present in the same form in every one of the three weighings made in the course of a determination.

When the oxide was dissolved the flask was kept at a temperature of 105° to 110° in the furnace already described while the solution water was carried off in a current of air from the purifying train, or in one case, in a current of dry hydrogen chloride. The chloride exhibited a tendency toward supersaturation. On this account hydrogen chloride was substituted for the air when it was judged that the saturation point was about to be reached. After the solution was saturated with hydrogen chloride, the furnace was removed and the flask was allowed to cool until the chloride began to crystallize out. Usually supersaturation had occurred at this lower temperature and the chloride came out in a solid mass. On warming the flask in the furnace, most of the chloride redissolved. Some crystals remained, however, and this prevented further supersaturation. As the crystallization progressed the flask was agitated so that the crystals as they formed at the surface would settle and a crust be prevented from forming over parts of the solution. Previous work done in this laboratory has indicated that the greatest danger of getting

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[1] Stein, Z. anorg. Chem., 55, 159 (1907)

a basic chloride instead of a normal salt lies at this point. If solution water remains and the temperature is subsequently elevated to the point where the first five molecules of water of hydration are driven off, hydrolysis is very likely to occur.

After the solution water was all removed the temperature was gradually raised to 125° but was not permitted to exceed 130°. At this point five molecules of water of hydration were lost rapidly. Dehydration was also found to take place quite rapidly at 110°-115°, but there was no danger in heating the chloride at the higher temperature provided no solution water had been enclosed. After condensation of moisture in the exit tube ceased, the temperature was slowly elevated to 200°-210°, where the pressure of aqueous vapor from the mono-hydrated chloride becomes high enough for the last molecule of water of hydration to disappear rapidly. After condensation in the exit tube had once more ceased the temperature was allowed to rise gradually to 350°-360°. This temperature was maintained for an hour to an hour and a half to make sure that all traces of moisture be driven off. The furnace was then heated to dull redness, after which the furnace was removed and the current of hydrogen chloride stopped while the chloride was fused by means of a Bunsen burner. There appeared to be some volatilization of the chloride in this process but since no current of gas was passing it is very improbable that there was any loss in the short period of time required for the fusion. After the bulb of the flask had cooled somewhat, the neck and arm of the flask and the inlet and outlet tubes were heated in the flame to volatilize any ammonium salts

that might have collected on the flask during the time it was exposed to the air. The flask was protected from dust and the laboratory atmosphere by a case of wood and glass specially constructed for this purpose. This case could be kept closed during all the ordinary course of the dehydration and had to be opened only for brief periods of special manipulation.

After the flask was cool the hydrogen chloride atmosphere was displaced by a current of air from the purifying train.The air was run slowly through the flask from thirty to forty-five minutes. The flask was then removed from the train, the cap on the outlet tube being adjusted first, while the air current was still passing through the flask. With the caps in place, the flask was immediatly removed to the balance case where it was allowed to hang for a period of about two hours before weighing was begun. In the earlier determinations the flask was handled with a clean cloth while it was being disconnected from the train but this sometimes caused electrification of the flask. In the later determinations the flask was manipulated with a pair of crucible tongs provided with rubber grips shaped to fit the neck of the flask.

The weighing of the flask containing the fused chloride presented difficulties not heretofore encountered in this laboratory. A gradual but quite uniform gain in weight was observed if the flask was left in the balance case. It was suspected that moisture from the air was diffusing through the ground joints and being absorbed by the chloride. Accordingly in determination 2, after the gain in weight had been noted for a period covering

about eighteen hours, the flask was reattached to the train and heated in a current of hydrogen chloride, at a temperature of 250°-270°, for one and one half hours. A slight condensation of moisture occurred in the exit tube. The flask was again weighed. The weight had dropped somewhat but had not returned to that found when the first weight was taken. The weight also commenced to rise again.

After this determination all the ground joints of the reaction flask were carefully reground with the finest abrasive used in grinding joints. At the end of this operation the joints were found to be tight according to the ordinary tests. A little concentrated sulphuric acid was placed in the flask and the flask suspended on the balance. The weight was taken at intervals and a slow but steady increase was still to be noted. In the next determination the weight of the flask containing the chloride was again found to rise gradually, though the increase was not quite as rapid as in the previous determination. The balance case could not well be supplied with a dry atmosphere without interfering with other work in which the same balance was used, so it was decided for the present to take the weight of the flask at as nearly as possible the same length of time after the flask was removed from the train in each determination. The error caused by the absorption of moisture would tend to give a low value. With a 0.5 gram sample of oxide the error would amount to about 0.1 in the atomic weight, in the time necessary for the flask to remain in the balance case. The error would be nearly constant, under average conditions of humidity, and does not vitiate the results of the determinations, since the

principal value of this series is in the comparison of the results of the different determinations.

The reaction flask was the same one used by Hopkins and Balke[1] in their determination of the atomic weight of yttrium, with the exception that the end of the exit tube, which was broken, was renewed. No difficulty was encountered in weighing yttrium chloride and Engle and Balke[2] report no difficulty in weighing dysprosium chloride. It is possible, though the close similarity between the various elements of the yttrium group would make it seem improbable, that erbium chloride absorbs moisture much more readily than either yttrium chloride or dysprosium chloride.

XII. DISCUSSION OF THE DETERMINATIONS-- Eight determinations were made. The data for all of these but the sixth are given below. In the sixth determination it was found that a small amount of basic chloride had formed. A small loss of material occurred in the process of redissolving this basic salt and dehydrating it again. The data for this determination is consequently omitted. In the other seven determinations the fused chloride dissolved to a clear solution in every case. In none of these determinations was it necessary to repeat the dehydration.

The solution of the fused chloride from one determination was tested with several indicators. Cochineal was lilac to purple; rosolic acid was pinkish yellow; methyl red was slightly yellowish; sodium alizarin sulphonate was red turning to purple; methyl orange was yellow; phenolphthalein was colorless;

1. Loc. cit. 2. Loc. cit.

and neutral litmus was red violet. This indicated the acidity[1] of the solution to be 10^{-6} to 10^{-7}.

In the tabulated data the second column shows the fraction of the nitrate fusion series from which the material was taken. A figure in parenthesis following indicates the determinatinn in which the same material was previously used. The third and fourth columns give the temperature and the length of time of ignition of the oxalate. The third column shows the number of hours the temperature was held at 775°-785° and the fourth the number of hours the ignition was continued at 875°-885°. The data follows:

Deter. No.	Fraction	Hours at 775°-785°	Hours at 375°-885°	Wgt. of Er_2O_3 In vacuo	Wgt. of Er O_3/ In vacuo	Ratio	Atomic Weight
1	34 M	8	---	0.86062	1.22899	.70027	168.47
2	34 M(1)	12	---	0.72202	1.03068	.70053	168.70
3	34 M	6	1	0.48901	0.69805	.70054	168.71
4	34 M(2)	6	1	0.48259	0.68876	.70067	168.84
5	34 L	10	1	0.50624	0.72285	.70034	168.54
6							
7	34 M(3&4)	7	3.5	0.81944	1.17074	.69994	168.16
8	34 L(5)	14	5	0.24325	0.34762	.69976	168.00

Note.- Oxide for No.7 was also heated for 9 hours at about 650° after the ignition at 875°-885°.

Examination of the data seems to show some connection between

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[1] Washburn - Principles of Physical Chemistry, pg. 333(1915)

the temperature and duration of the ignition of the oxide and the ratio obtained. After a number of determinations had been made it was suspected that this might be the case. Accordingly the ignition was prolonged in the later determinations, particularly at the higher temperature. The fifth determination showed somewhat of a drop in the ratio, and the seventh and eighth showed a greater fall. It will be noted that the results of the first two determinations do not appear to agree with this generalization. The low value for the first might be accounted for on the ground that the material had not been entirely purified from base elements. The same material, repurified, was used in the second determination. The effect of prolonged ignition in the last two determinations is striking, however, especially since the value for the ratio decreased in the face of the tendency it would have to rise on account of the distillation of platinum from the crucible into the oxide. The test for platinum which the chloride from these two determinations gave was described on page 29.

What change the prolonged ignition brought about was a matter of question. Hofmann[1] states that erbium oxalate is almost completely decomposed at 575° and that it is completely decomposed at 845°. He does not state the length of time required to effect complete decomposition at 845°. From this data it would seem probable, however, that the ignition of the oxalate in the earlier determinations should have been sufficient to give a complete decomposition to oxide. Hofmann does not state how the

[1] Ber. 43, 2631 (1910)

oxide for his oxide-sulphate ratio was prepared, but from his attention to the decomposition of the oxalate in this same investigation it may be inferred that the oxide was prepared by the ignition of the oxalate. If erbium oxalate is not completely decomposed at 845°, or even by heating at 875°-885° for three or four hours, Hofmann's oxide-sulphate ratio, upon which the present accepted value for the atomic weight of erbium is based , is immediatly thrown open to question.

An attempt was made to determine whether the oxide as prepared for the earlier determinations contained carbonate or occluded carbon dioxide. The combined residues from the determinations were purified in the usual manner and the oxalate ignited for seven hours at 775°-785° and two hours at 875°-885°. The oxide weighed 1.1 grams. It was introduced into the reaction flask and some recently boiled water added. The flask was attached to the train and a current of air passed through until no precipitate could be observed in lime water after the air had passed for an hour. The lime water was contained in a set of Geissler bulbs connected to one lead from a two-way stopcock attached to the waste gas tube leading from the exit of the flask. It was found that the solid potassium hydroxide did not remove all of the carbon dioxide from the air. The air was therefore first bubbled through a bottle of sodium hydroxide solution and through sodium hydroxide substituted for the dilute sulphuric acid in the first tower of the purifying train. When no precipitation was observed in the Geissler bulbs after the air had passed for an hour the current was directed through

the other lead of the two-way stopcock into another set of Geissler bulbs containing lime water. About 3 c.c. of concentrated sulphuric acid was then introduced into the flask by loosening the inlet tube slightly. The air current had to be stopped while the acid was allowed to run from a pipette through the loosened joint. No carbon dioxide could enter, however,for the acid itself sealed the joint. The inlet tube was then readjusted and the current of air continued. Owing to the slight solubility of the sulphate it was difficult to tell when all the oxide had been converted. Accordingly the passage of the air was continued for four hours while the flask was heated to 120°-125°. At the end of this time there was some precipitate in the lime water but it was not certain whether this was caused by carbon dioxide expelled from the flask or by traces of carbon dioxide remaining in the air from the train.

Since the results of the experiment just described were somewhat uncertain, it was decided to repeat the test, using nitric acid instead of sulphuric acid. The material from the foregoing test was repurified in the usual manner except that the precipitation with ammonia was omitted. The oxalate was ignited for eight hours at 775°-885°. Air was swept through the train for an hour and a quarter before the nitric acid was added. No precipitate formed in the lime water. After the acid was added the temperature was kept below 100° to avoid carrying much acid into the absorption bulbs. A drop of phenolphthalein was added to the lime water to show whether it remained alkaline. It did so during the hour that was needed for the

complete solution of the oxide. At the end of this time a distinctly noticeable amount of precipitate had formed. After the flask was removed the air from the train was again tested for carbon dioxide. No precipitate formed in an hour and a half.

It is thus evident that erbium oxide, prepared from the oxalate and ignited for eight hours at a temperature slightly below 800° still contains quite an amount of carbonate or occluded carbon dioxide. The test made using sulphuric acid indicates that this is probably true also for oxide heated an extra two hours at a temperature 100° higher. This is born out by the lower ratios obtained in the seventh and eighth determinations, in which the ignition at 875°-885° was continued still longer. This fact may have some bearing on the general tendency of the oxide-chloride ratio to give values higher than those obtained by other methods. The matter of securing an oxide which shall be pure and of definite composition will be further investigated for all the elements to which the oxide-chloride ratio has been applied. It is obvious also that this will have to be taken into consideration in the oxide-sulphate ratio or any other ratio if oxide is used which is prepared by the ignition of the oxalate.

XIII. SUMMARY OF RESULTS.

1. A comparative study was made of the newer methods proposed for the separation of erbium and yttrium. The cobalticyanide and nitrite precipitation methods were found to give good results. The latter was the more efficient and practicable.

2. The classic nitrate fusion method was found to give results far superior to the other methods which were studied.

3. Erbium material of very high purity was prepared by the nitrate fusion method.

4. The ratio of erbium oxide to erbium chloride was determined in seven analyses. The ratio was found to vary with the temperature and length of time of ignition of the oxide.

5. Erbium oxide, prepared by the ignition of the oxalate and ignited for several hours at nearly 800° and two hours at nearly 900°, was found to retain appreciable amounts of carbon dioxide.

VITA.

The author received his early education in the public schools of Zeeland, Michigan. He also attended the public High School of that place. He attended Hope College from 1909 to 1913, receiving the degree of Bachelor of Arts from that institution in 1913. During the school years 1913-14 he was Graduate Assistant, and in 1914-15 Assistant, in Chemistry in the University of Illinois, from which the degree of Master of Science was received in 1915. The author continued his work in the Graduate School at Illinois during the years 1915-16 and 1916-17, holding a Fellowship in Chemistry during the latter year.

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